Report for 2003WY10B: Geochemistry of CBM Retention Ponds Across the Powder River Basin, Wyoming

Publications

- Conference Proceedings:
    - Jackson, R.E., K.J. Reddy, R.E. Olson, and D.E. Legg, 2004. Geochemistry of coalbed methane disposal ponds across the Powder River Basin, Wyoming. In Proceedings of Society of Range Management 2004 Annual Meetings, Salt Lake City, Utah.
    - Jackson, R.E., K.J. Reddy, R.A. Olson, and D.E. Legg, 2005. Geochemistry of Coalbed Natural Gas Product Water across Five Wyoming Watersheds. In Proceedings of Soil Science Society of America 69th Annual Meetings. Salt Lake City, Utah.

Report Follows

Abstract

The Wyoming Water Research Program (2003) funded a project to study geochemical changes of coalbed natural gas (CBNG) disposal pond waters across the Powder River Basin (PRB) in collaboration with the US Geological Survey and the Wyoming Water Development Commission. Objectives of this research were to monitor the geochemical changes and water quality of CBNG disposal ponds in Tongue River Basin (TRB), Powder River Basin (PRB), Little Powder River Basin (LPRB), Belle Fourche River Basin (BFRB), and Cheyenne River Basin (CRB) over a period of 3 years. This report summarizes final results of the project from March 2003 to August 2005. The CBNG product water samples from discharge points and corresponding disposal ponds were collected during the summer months of 2003, 2004, and 2005. In addition, sediment, macroinvertebrate, and plant community composition samples were collected from the CBNG disposal ponds. Water samples were analyzed for pH, dissolved oxygen (DO), electrical conductivity (EC), major cations (e.g., Ca, Mg, Na, and K), major anions (e.g., alkalinity, sulfate, chloride, fluoride, nitrate, and phosphate), and trace elements (e.g., Al, As, Ba, B, Fe, Cd, Cu, Cr, Mn, Mo, Se, Pb, and Zn). Sodium adsorption ratio (SAR) was calculated from the measurements of Ca, Mg, and Na. Results identify how quality of CBNG discharge and disposal pond waters change, predominantly salt concentration, SAR, and trace metals as a function of watershed physical and chemical characteristics. CBNG pond sediment fractionation analysis for 2003, 2004, and 2005 indicate Fe is primarily bound in Fe/Mn oxide sediment fraction, Ba is in exchangeable and carbonate bound fraction, As is Fe/Mn oxide but increasing in exchangeable fraction between years, and Se is in organic fraction. Macroinvertebrates were more abundant and have higher taxa richness in CHR, BFR, and LPR watersheds than in PR and TR watersheds. Similarly, there were more vegetation species encountered in and around ponds in CHR, BFR, and LPR watersheds than in PR and TR watersheds. Water quality data of CBNG produced water obtained over three year period was summarized and disseminated to participating local landowners. Results of this research help water users (landowners, agriculture and livestock producers, and ranchers) and water managers (state, federal, and local agencies) with the planning and management of CBNG product water across five major watersheds of the Powder River Basin.

Statement of Critical Regional or State Water Problems

Demand for natural gas (methane) is increasing within the United States because of the energy shortage. Further, methane is a clean form of burning fossil fuel. Several states within the United States (e.g., Wyoming, Colorado, Montana, New Mexico, and Utah) are exploring methane extraction from their coal resources. As an example, in the Powder River Basin (PRB) of Wyoming, it is estimated that there are 31.7 trillion cubic feet of recoverable CBM (coalbed methane). Currently, the CBM development in this basin is occurring at a rapid pace as demand for natural gas has increased in the United States (DeBruin et al., 2000).

Methane is formed deep in confined coalbed aquifers through biogeophysical processes and remains trapped by water pressure. Recovery of the methane is facilitated by pumping water from the aquifer (product water). It is estimated that a single CBNG well in the Powder River Basin may produce from 8 to 80 L of product water per minute, but this amount varies with aquifer that is being pumped and the density of the wells. At present, more than 16,000 wells are under production in the PRB and this number is expected to increase to at least 30,000. Based on information provided by the Wyoming Geological Survey, approximately 2 trillion L of product water will eventually be produced from CBNG extraction in Wyoming. Commonly 2 to 10 CBNG extraction wells are placed together in a manifold system discharging to a single point and releasing into constructed unlined disposal ponds. These disposal ponds are constructed with initial well pumping. The Wyoming DEQ considers this water as surface water of the state with Class 4C designation.

Various metals such as Fe, Ba, As, and Se in the CBNG pond waters are expected to go through several geochemical processes including desorption and dissolution, ion complexation (speciation), and adsorption and precipitation. These processes in turn control the quality of product water in disposal ponds as well as the water that is infiltrating into the shallow ground water. Very little information is available on the geochemistry of CBNG product water and associated disposal ponds in the Powder River Basin (Rice et al., 1999; McBeth et al., 2003a and b). The studies conducted by Rice et al. (1999) only examined the chemistry of CBNG discharge water at wellhead. McBeth et al. (2003a and b) studies examined the chemistry changes of product water both at wellhead and in disposal ponds of the Powder River Basin. However, to our knowledge no studies involved

the monitoring of the geochemical processes that product water undergoes in disposal ponds across the Powder River Basin. The CBNG product water discharged to the surface is managed and regulated by several state and federal agencies. To effectively manage this water resource there is a need to understand the geochemical changes that occur in CBNG disposal ponds over time. This final report outlines results accomplished from data collected from March 2003 to August 2005. This report consists of objectives, methods and procedures, site selection, sample collection and analysis, results, clientele network, presentations, and student education and training.

Objectives

The overall objectives of this research are to:

1.   Collect, analyze, and monitor pH, DO, EC, DOC, major cations (e.g., Ca, Mg, Na, and K), major anions (e.g., alkalinity, SO_4^{2-}, Cl^-, F^-, NO_3^-, and PO_4^{2-}), and trace elements (e.g., Al, As, Ba, B, Fe, Cd, Cu, Cr, Mn, Mo, Se, Pb, and Zn) from produced water samples at discharge points and disposal ponds over a period of 3 years (2003, 2004, 2005);

2.   Identify statistical differences of produced water test parameters between discharge points and associated ponds;

3.   Identify statistical differences of produced water test parameters between watersheds of a particular water type (wells and ponds);

4.   Predict geochemical changes (speciation, adsorption, and precipitation) for critical metals such as Fe, Ba, As, and Se in the disposal pond from produced water and associated disposal pond sediment;

5.   Identify trends in major cation, major anion, and trace element concentrations of produced water at discharge points and associated ponds;

6.   Compile a list of aquatic macroinvertebrate and wetland plant species associated with disposal ponds; and

7.   Transfer research results to user groups through project demonstrations, workshops, and local meetings.

Methods and Procedures

Site Selection

        We selected twenty-six sites within five Wyoming watersheds to obtain CBNG well and associated pond data. Site selection was coordinated with a network of working partners. These working partners include: Wyoming Department of Environmental Quality (WY-DEQ), Wyoming Water Development Commission (WY-WDC), Coalbed Methane Industry, Wyoming Landowners and Citizens, U.S. Geological Survey (USGS), Wyoming State Geological Survey (WYSGS), U.S. Environmental Protection Agency (USEPA), Colorado, and Montana. We sampled seven sites in each of the Little Powder River (LPR) and Powder River (PR) watersheds. We sampled three sites from Cheyenne River (CHR) watershed and four sites from Belle Fourche River (BFR) watershed, and five sites from Tongue River (TR) watershed (Figure 1).

Sample Collection and Analysis

        Before sample collection, a pilot study was conducted to determine sampling location within the CBNG pond waters. Chemical, plant, and aquatic macroinvertebrates were also examined to determine the sampling locations to obtain a representative sample. CBNG water samples from each well and corresponding ponds were collected during the summer of 2003. Before sample collection, field measurements including pH, conductivity, temperature, ORP, and dissolved oxygen were taken in each well and pond.

        CBNG water samples from each discharge well and corresponding pond were collected once during the summers of 2003, 2004, and 2005. Before sample collection, field measurements including pH, conductivity, temperature, ORP (oxidation and reduction potential), and dissolved oxygen were taken from each CBNG discharge well and associated pond with an Orion Model 1230 Multi-Probe. Exact locations for pond measurements were taken directly away from discharge well, and were chosen upon pH stabilization at different distances from discharge point.

        Duplicate water samples of discharge wells and ponds were taken from each site. Samples were transported in ice coolers (2° C) to the University of Wyoming Water Quality Laboratory. Each sample was filtered through 0.45µm filter and subdivided: half were acidified to pH of 2.0 with HNO_3, and half were left unacidified. Acidified samples were analyzed for Ca, Na, Mg, K, Fe, Al, Cr, Mn, Pb, Cu, Zn, As, Se, Mo, Cd,

Ba and B by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and unacidified samples were analyzed for SO_4^{2-}, Cl^-, F^-, NO_3^-, and PO_4^{3-} using Ion Chromatography (IC). Total alkalinity on unacidified samples was determined by acid titration method.

The geochemical model MINTEQA2 was used to verify analytical data accuracy and to calculate ion activities (Brown and Allison, 1992). This model uses chemical data, pH, ORP, alkalinity, and redox couples to calculate ion activities, ion complexes, and saturation indices. Sodium adsorption ratios were calculated from Ca, Na and Mg concentrations (Hanson et al., 1993).

The quality control/quality assurances protocols such as duplicate sampling and analysis, trip blanks, and known concentrations of reference standards were included. Standard laboratory procedures were used for all analytical analyses and pH, electrical conductivity, and alkalinity measurements (APHA, 1992). All analyses were performed following CFR 40, Part 1, Chapter 36 procedures (WYDEQ, 2001).

Three statistical tests were used to identify differences between CBNG water samples. Due to a "natural pairing" of the discharge well and associated discharge pond, paired t-tests were used to identify these differences between water types (discharge wells vs. associated ponds) (alpha = 0.05; SAS, 2000). A 5x3 factor analysis was used to identify element differences of a particular water type between watersheds and years, and an analysis of variance with a Tukey mean separation test was used to further identify element differences between years within specific watersheds (alpha = 0.05; SAS, 2000. A simple linear regression was conducted to predict discharge pond SAR from discharge well SAR using MiniTab 13.1 (2000) computer software.

Disposal pond sediments were collected during the summer of 2003, 2004, and 2005 using 4.5cm diameter PVC corer. Sample locations are located directly away from discharge well and were chosen upon pH stabilization at different distances from discharge point. Typically, sediment was collected approximately 3 meters from discharge point and consists of a 20cm core. A sediment core was taken from every pond, placed in a 1L polypropylene bottle, and then completely filled with pond water. Once at the lab, all samples were frozen. Two samples from each watershed (10 total samples) were separated into exchangeable, carbonate bound, Fe/Mn oxide bound, organically bound, and residual mineral fractions to determinate the fate of As, Ba, Fe, and Se. Each fraction was dissolved in an appropriate solution and extracted. The extract was then analyzed for As, Ba, Fe, and Se on ICP-MS as described by Tressier et al. (1979).

Since Wyoming and surrounding states do not have sampling protocols for macroinvertebrates in lentic systems, a minimal effort approach for sampling was selected. Four macroinvertebrate samples (collected from the four cardinal directions) were collected from the water column using a D-net with 1mm mesh and from sediment using an 8cm diameter core sampler. Water column samples were combined as well as sediment samples to form a composite sample for the water column and sediment column for each pond. Samples were taken from 2 ponds in each different watershed (20 total samples) and preserved in 95% ethanol. At the laboratory, samples were sorted from vegetation and debris, and preserved in 75% ethanol (Merrit and Cummins, 1996). Aquatic macroinvertebrate samples were sent to a certified laboratory specializing in analysis of aquatic macroinvertebrate communities (Aquatic Biology Associates, Inc) for identification to lowest taxonomic level. Laboratory data included total taxa present and community richness. Vegetation identification was performed on location for predominant wetland and aquatic plant species in and around ponds. Samples of unknown species were collected and brought back to the lab for identification.

Task Completion List
2003, 2004, and 2005 Sample Seasons
- Water chemistry completed for all samples (anions, cations, trace metals, DOC)
- MinteqA2 modeling completed
- Statistical analysis completed (T-tests, Factorial Analyses, ANOVAs, and Regressions)
- Compiled CBNG water quality data and contacted participating landowners of results
- Aquatic macroinvertebrate samples analyzed
- Vegetation species list completed
- Sediment Fractionation analysis for all 3 years
- Project results were disseminated to the public through local, regional, and national meetings and workshops

Results and Discussion

All element concentrations are averages from duplicate samples. Specific chemical concentration, statistical analyses, and complete data and analyses will be in Rich Jackson's PhD. Dissertation. Results suggest that discharge wells are chemically different from corresponding discharge ponds (Figures 2, 3, 5, and 6). Discharge well pH is stable and controlled by the geologic formation and the concentration of dissolved CO_2 confined in the aquifer (Patz et al., 2004). Discharge well pH varied between 6.9 and 7.9. Discharge pond pH is much more varied (between 7.6 to 9.6) because of the degassing of CO_2 from the produced water and its interaction with local watershed soils (McBeth et al., 2003a). Total dissolved solids also increased from discharge well to ponds throughout all watersheds. The TDS increased from 391mg/L in the Cheyenne discharge wells up to 1588mg/L in the Powder, then leveled off in the at 1200mg/L in the Tongue. This similar trend was also observed in the discharge ponds, lowest TDS in Cheyenne at 373mg/L and the highest in the Powder at 1760mg/L. Salts and TDS increased from discharge wells to ponds due to evaporation. Sodium adsorption ratio increase from discharge well to pond, and increased between watersheds (Figure 3).   Lowest SAR values were in Cheyenne discharge wells at 5.8, and the highest were in Tongue discharge wells at 47. Discharge pond SAR values in the Tongue should be greater than their corresponding ponds, but these CBNG product waters are commonly acidified with Sulfur Burners. Sulfur Burners convert sulfur pellets into sulfuric acid and mix with discharge well water before entering the discharge pond. The "acidification" lowers discharge pond pH and alkalinity, causing many of the carbonates to dissolve, artificially increasing Ca and Mg. Since SAR is a ratio between Na / Ca and Mg, this process lowers SAR. Since discharge pond water was chemically changing as a function of watershed chemistry, we predicted SAR of pond water using a regression model (Figure 4). The predicted discharge pond water results suggested a high correlation ($R^2 = 0.83$) to discharge well SAR.

Trace metal results also suggest that discharge wells are chemically different from corresponding discharge ponds (Figures 5, and 6). Iron concentrations varied between years and watersheds with no apparent trend. Highest Fe concentrations were in Tongue discharge wells (40µg/L), while the highest was in Belle Fourche ponds at 683µg/L. Discharge ponds had typically higher Fe concentrations than the discharge wells. Aluminum followed a similar trend as Fe, except in 2003 with Tongue discharge well water. Acidification from Sulfur Burner treatment lowered the pH of discharge well water, causing Al to become soluble. For example, Al concentrations were 10µg/L at discharge wells, and increased to 4300µg/L after acidification. Otherwise, Fe and Al concentrations are primarily controlled by the geologic formations of the individual watersheds. Barium decreased from discharge well to discharge ponds across all watersheds. Highest Ba concentrations were in Little Powder discharge wells at 690µg/L and the lowest concentrations were in Tongue discharge ponds at 102µg/L. These results suggest that Ba is precipitating out in the discharge ponds. Arsenic concentrations increased from discharge well to discharge pond across all watersheds. Discharge well Arsenic concentrations ranged from non-detectable to 2.3µg/L, while discharge ponds ranged from 0.2µg/L to 22.9µg/L. These results suggest that arsenic is concentrating in discharge ponds. Selenium had low concentrations in both discharge wells and ponds. Selenium ranged from 0.1µg/L in discharge well to 2.6µg/L in discharge pond.

CBNG discharge pond sediment fractionation results for Fe, Ba, As, and Se in 2003, 2004 and 2005 are presented in figures 7 and 8. Iron concentrations don't vary much between years, but do vary between watersheds. The Fe/Mn Oxide bound fraction of Fe in BFR was the highest between all watersheds in 2003 (254mg/L), but decreased in 2005 (75mg/L). Variable Fe/Mn Oxide bound Fe is expected due to changes in soils and sediment mineralogy among the different watersheds. The Fe/Mn oxide bound fraction had the highest Fe concentration between all watershed and all years. Barium concentrations in all sediment fractions were low (1 to 9.5mg/L), but exchangeable and carbonate bound were the dominant fractions between all years and all watersheds. There is a slight decrease in Ba concentrations from 2003 to 2005 in exchangeable and carbonate bound fractions. Pond sediment As had the highest concentrations bound in Fe/Mn oxide fraction between watersheds and years, but exchangeable and carbonate bound fractions of As increased between years. In 2005, exchangeable and carbonate bound fractions of As were between 5 and 27.5µg/L compared to 0.5 and 21µg/L in 2003. The Fe/Mn oxide bound fraction appeared to decrease from 2003 to 2005. Selenium concentrations in all fractions were low between watersheds and years. Organic bound Se fraction was the dominant fraction, with exchangeable Se fraction increasing from 2003 to 2005.

Figure 9 identifies aquatic macroinvertebrate community assemblages for 2003, 2004, and 2005. Collector-gatherers and predators are the most represented functional feeding groups in all watersheds. Macroinvertebrate communities may be a function of the age of discharge pond and the relative wetland vegetation that is present. Table 1 identifies vegetation encountered in and around discharge ponds across all five watersheds. More vegetation species were observed in and around CHR, BFR, and LPR discharge ponds than in PR and TR discharge ponds. This may be a function of pond age.

Conclusions
Results from this study suggest the following:
- Discharge well water is chemically different than associated discharge pond water across watersheds,
- Watersheds (CHR, BFR, LPR, PR, and TR) examined in this study are chemically different from each other,
- During monitoring years from 2003 to 2005, TR, PR, and to some extent LPR were more chemically reactive when compared to CHR and BFR.
- Since discharge pond water was chemically changing as a function of watershed chemistry, we predicted SAR of pond water using regression model. The predicted discharge pond water results suggested a high correlation ($R^2 = 0.83$) to discharge well SAR.
- Monitoring studies also suggested that SAR of pond water increased between years due to decrease in Ca concentration, except for TR. In TR, produced water is chemically treated to add Ca and to lower SAR.
- Many trace metals increase and accumulate from discharge well to discharge pond. This could become a problem after many years of continual discharge and will require remediation.
- Fe, Ba, and Se are bound in Fe/Mn oxide and organic fractions of CBNG pond sediment and pose little hazard. The As concentration is increasing in exchangeable and carbonate bound fractions, which are can be readily bioavailable and may pose a hazard with continued CBNG discharge.
- Knowledge transfer between university personnel, state/federal agencies, and local landowners is successful when local landowners are given the option to participate and assured anonymity of data collection locations on their property.
- Results of this project are helping WY-DEQ in issuing CBNG discharge permits and local landowners in management of CBNG produced water on their property.

Student Support
Rich Jackson, Ph.D. student, majoring in Rangeland Ecology and Watershed Management and Water Resources
Michelle Patterson, graduate student in Rangeland Ecology and Watershed Management and Water Resources
Jonathan Anderson, graduate student in Soils
Cotton Bousman, graduate student in Rangeland Ecology and Watershed Management
Amy Groenkie, Soils Department Technician
Keri Bousman, undergraduate student in Rangeland Ecology and Watershed Management
Don-O-Lynn Weed, SRAP high school student participant
Cynthia Milligan, graduate student in Rangeland Ecology and Watershed Management

Awards
- James B. Warner Scholarship (2004) from the American Water Works Association
- Best Oral Presentation (2004) from University of Wyoming Graduate School

Clientele Network
Several contacts were made with different clientele groups to obtain access to the sampling sites and permission to collect samples. These contacts or clientele included WY-DEQ, WY-WDC, CBNG Industry, WY Landowners and Citizens, NRCS personnel, Conservation District personnel, WY Cooperative Extension

Agency, USGS, EPA, Colorado, Montana. Annual meetings along with water quality reports were accomplished for 2003, 2004 and 2005 with individual landowners who participated in this project. Annual presentations were given to Wyoming Water Development Commission as well as Basin Advisory group meetings (Kaycee, 2003 and New Castle, 2006). Information from this project was also disseminated in national and international meetings (Soil Science Society Meetings 2003 and 2005) and regional meeting (Range Society Meetings 2004, CBNG Research, Monitoring, and Applications Conference 2004).

Presentations
1. Wyoming Water Development Commission Basin Advisory Group Meeting, April 13th 2006 New Castle, Wyoming.
2. Soil Science Society of America 69th Annual Meetings, November 7th 2005. Salt Lake City, Utah.
3. Wyoming Water Development Commission Annual Meetings, December 4th, 2004, Cheyenne, Wyoming.
4. 1st Annual Coalbed Natural Gas Research, Monitoring, and Applications Conference. Aug 17-19, 2004. Laramie, Wyoming.
5. University of Wyoming 2003 Graduate Student Symposium March 2nd, 2004, Laramie, Wyoming. This presentation won Best Project Presentation Award.
6. USDA-CSREES National Water Quality Conference: Integrating Research, Extension and Education scheduled January 11-14, 2004 in Clearwater, Florida.
7. Wyoming Water Development Commission Annual Meetings, December 4th, 2003, Cheyenne, Wyoming.
8. Rangeland National Annual Meetings, Water Quality Division, scheduled January 24-30, 2004 in Salt Lake City, Utah.
9. American Society of Agronomy (Soil and Water Ecology Section) Meetings, Denver, Colorado. November 5, 2003
10. Wyoming Department of Environmental Quality Meeting, Cheyenne, Wyoming. August 21, 2003.
11. EPA-USGS Meeting for Tongue River and Powder River Long-term Monitoring Network. Sheridan, Wyoming. June 5, 2003
12. Missouri River Basin Natural Resources Meeting, Benedictine, Kansas. June 2-4, 2003 (invited).
13. American Society of Surface Mining and Reclamation Symposium, Billings, Montana. June 5-6, 2003.
14. Wyoming Water Development Commission, River Basin Advisory Group Meeting, Kaycee, Wyoming. June 16, 2003.
15. Wyoming Department of Environmental Quality (Water Quality Division) Meeting, Cheyenne, Wyoming. May 10, 2003. This meeting included represents from U.S. EPA Region VIII, BLM, CBM Industry, Colorado State University.

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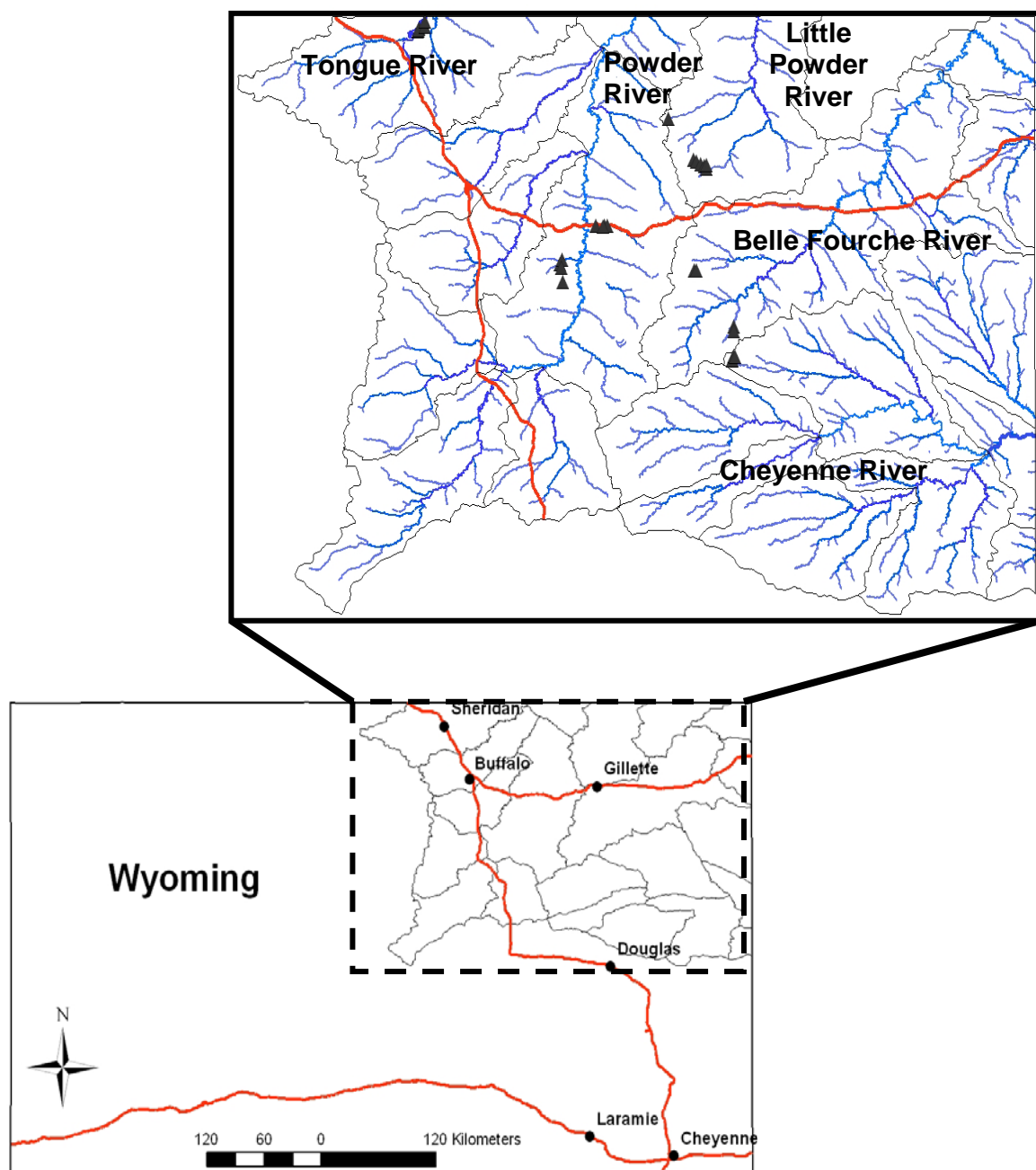
Figure 1. Sample site locations in the Powder River Basin, Wyoming.
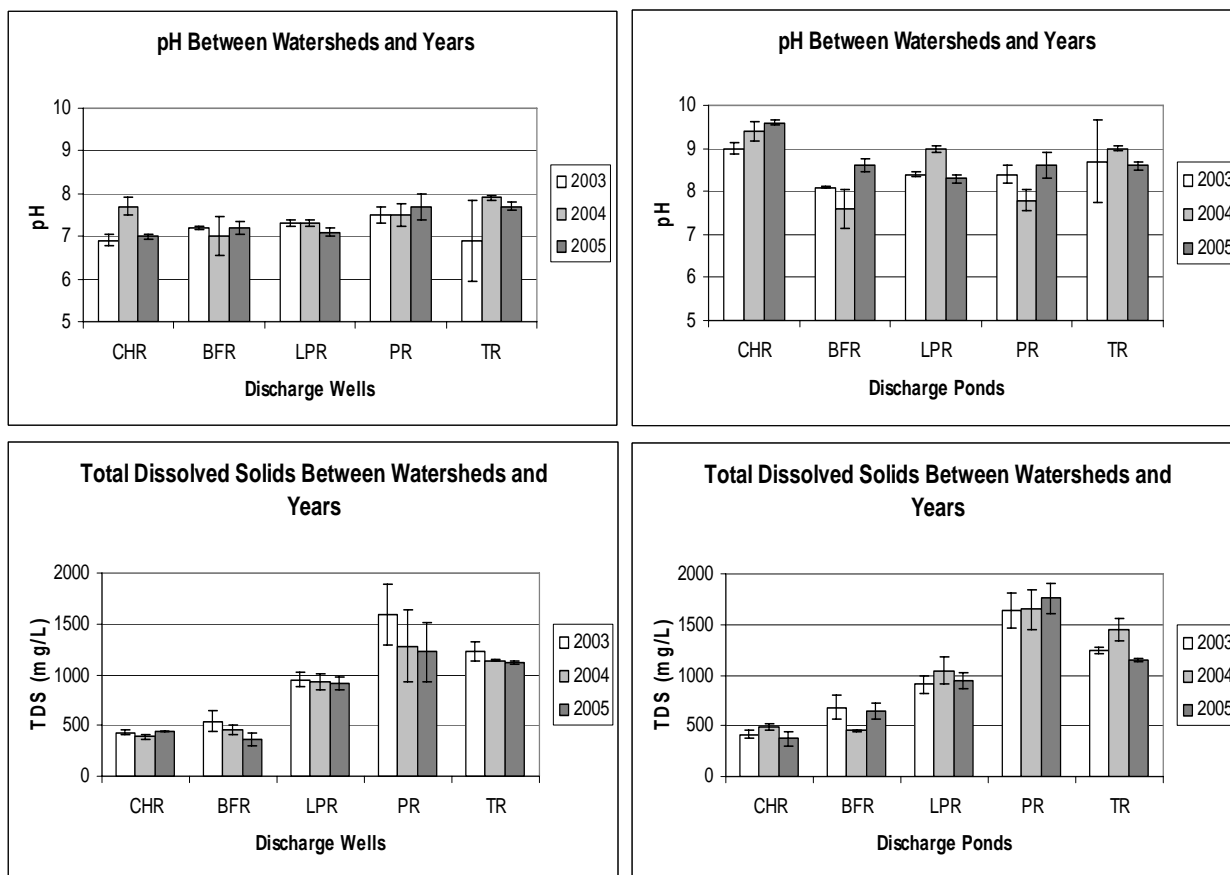
Figure 2. CBNG discharge wells and ponds pH and Total Dissolved Solids (TDS) between Cheyenne, Belle Fourche, Little Powder, Powder, and Tongue River watersheds from 2003 to 2005.
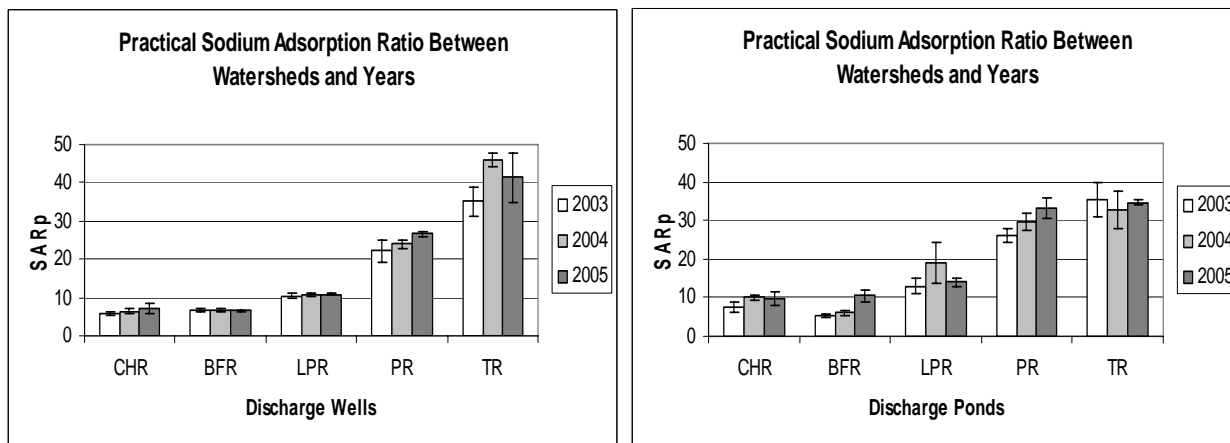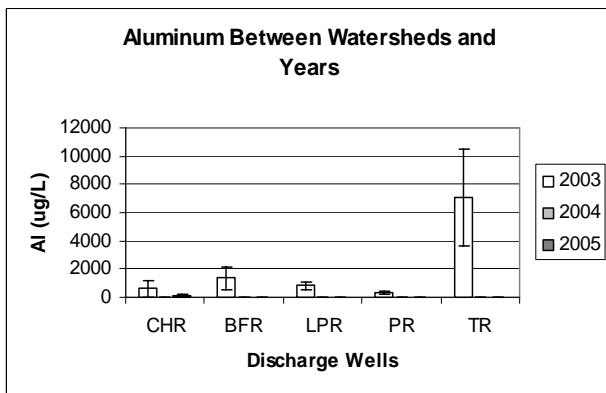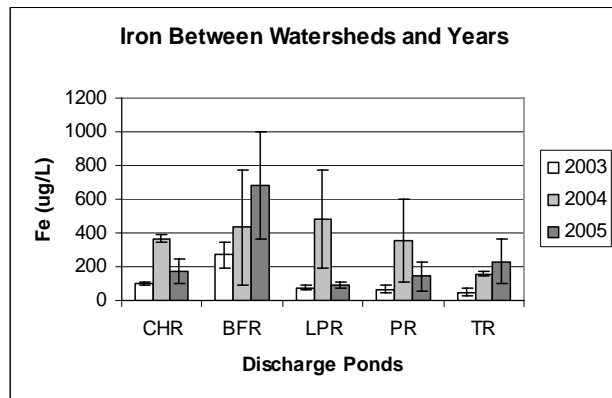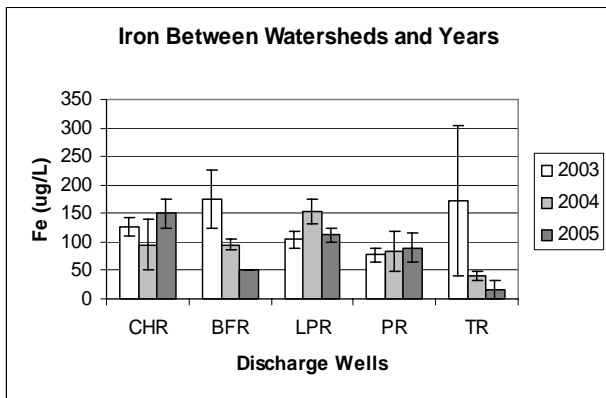
Figure 3. CBNG discharge wells and ponds Sodium Adsorption Ratio between Cheyenne, Belle Fourche, Little Powder, Powder, and Tongue River watersheds from 2003 to 2005.
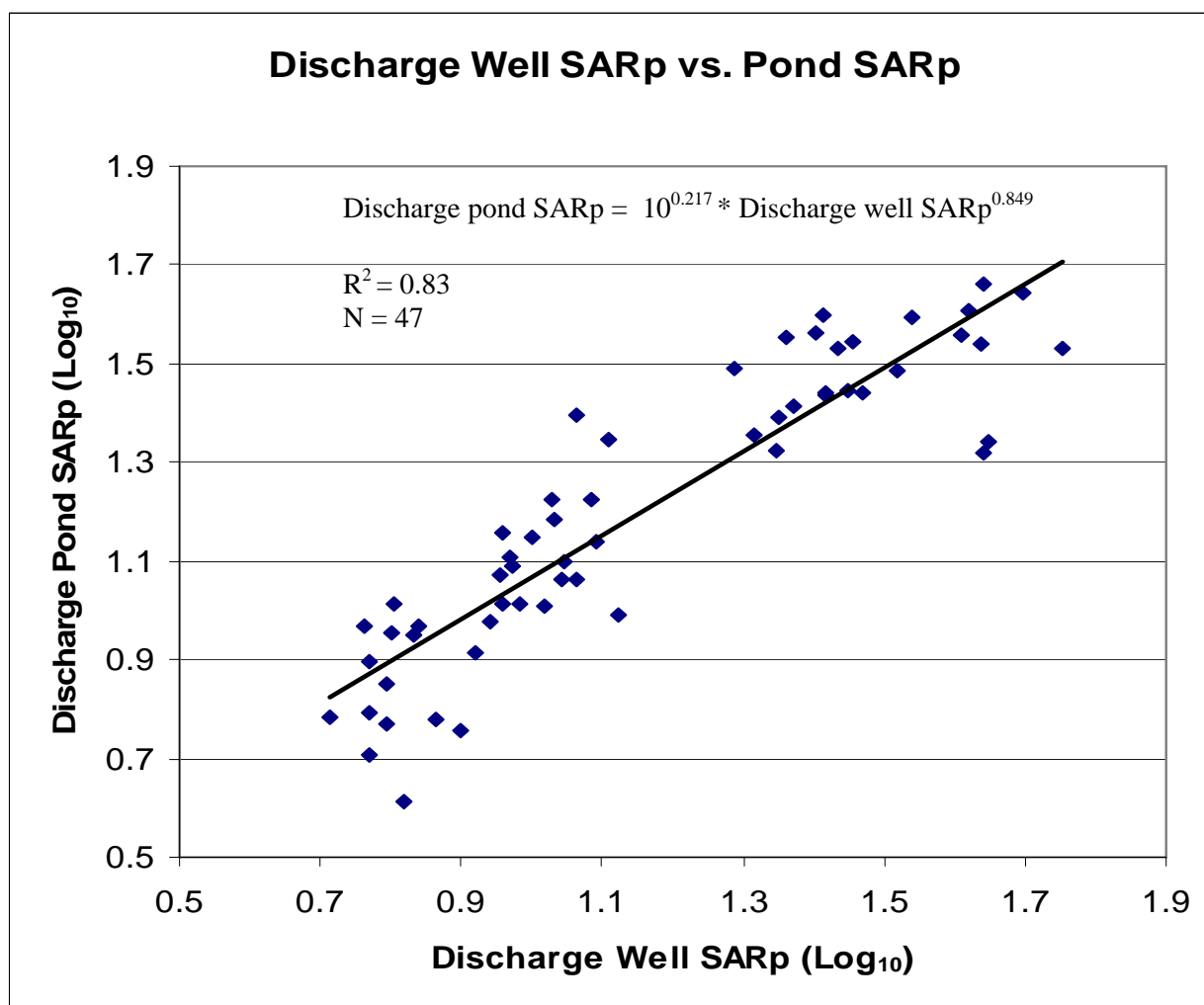
Figure 4. Linear regression between CBNG discharge well SAR and discharge pond SAR.
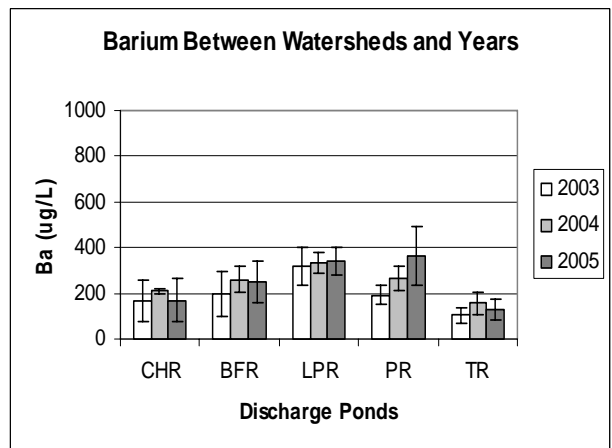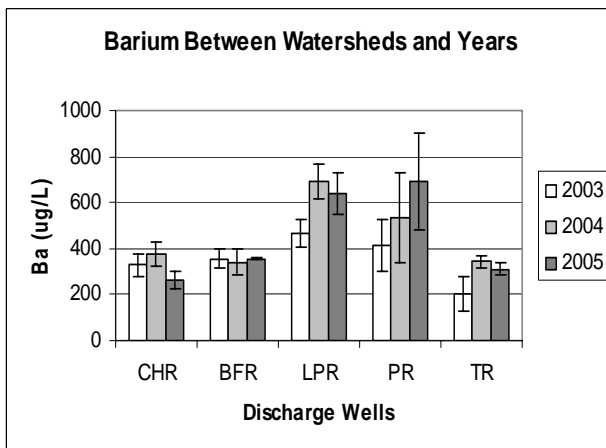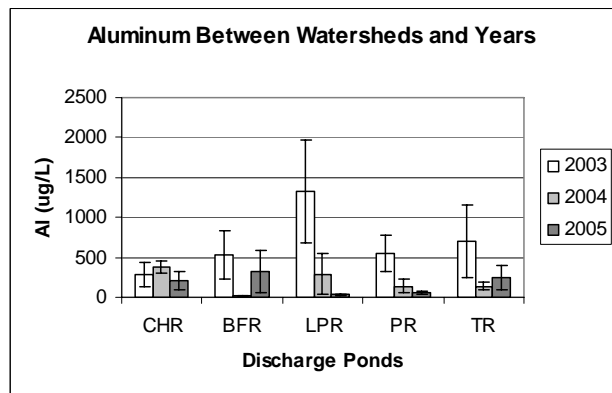
Figure 5. CBNG discharge wells and ponds iron, aluminum, and barium concentrations between Cheyenne, Belle Fourche, Little Powder, Powder, and Tongue River watersheds from 2003 to 2005.
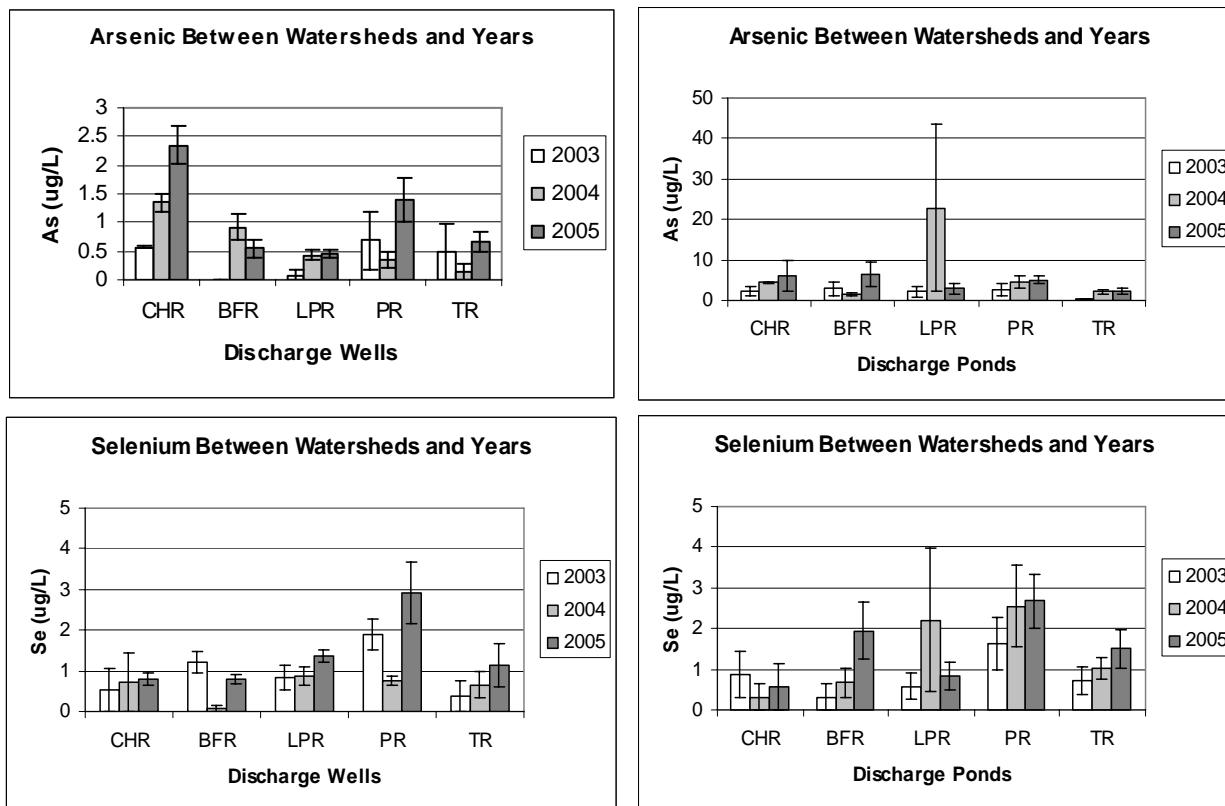
Figure 6. CBNG discharge wells and ponds arsenic and selenium concentrations between

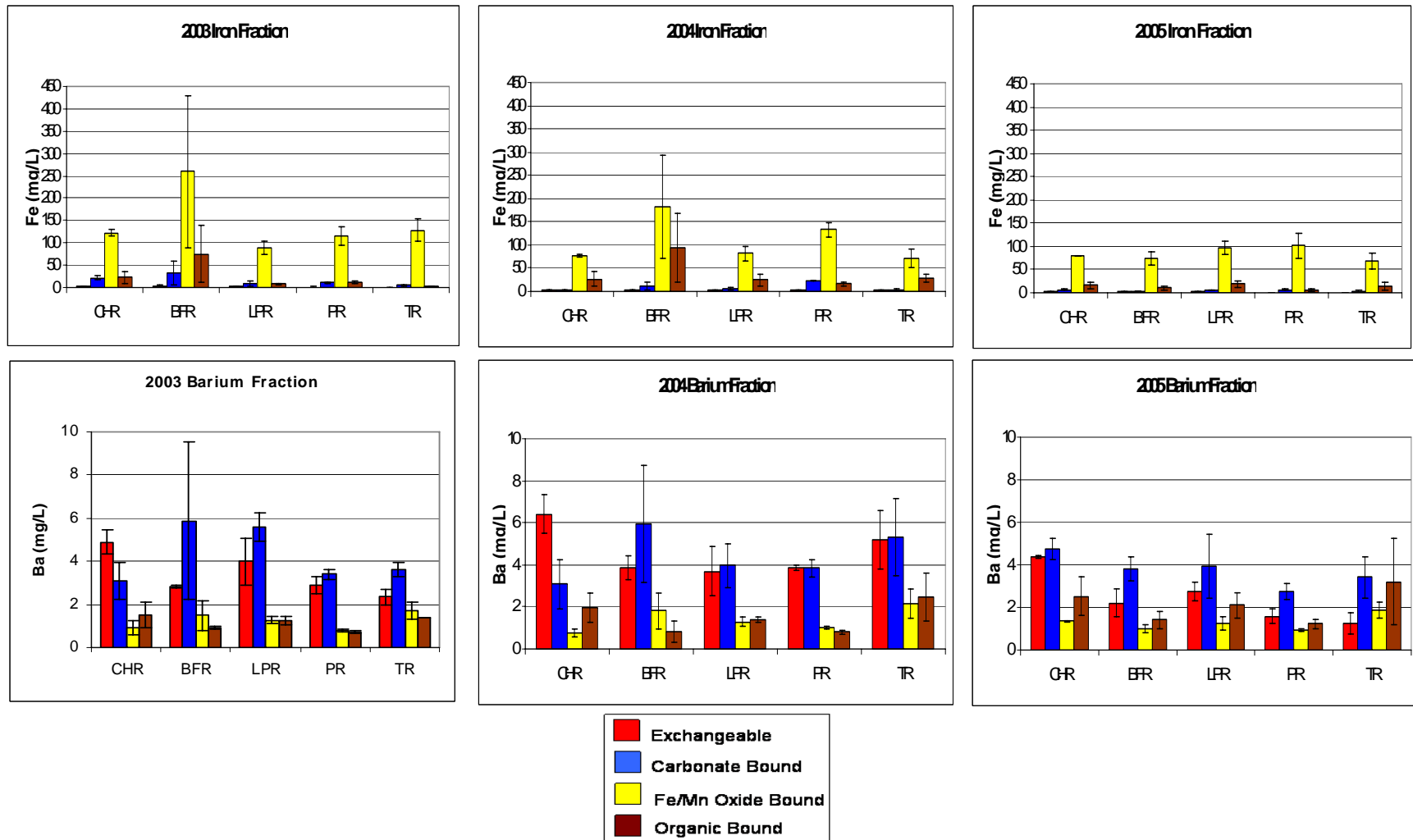Cheyenne, Belle Fourche, Little Powder, Powder, and Tongue River watersheds from 2003 to 2005.

Figure 7. Average Iron and Barium concentrations in Exchangeable, Carbonate bound, Iron/Manganese Oxide bound, and Organic bound fractions of CBNG discharge pond sediment.
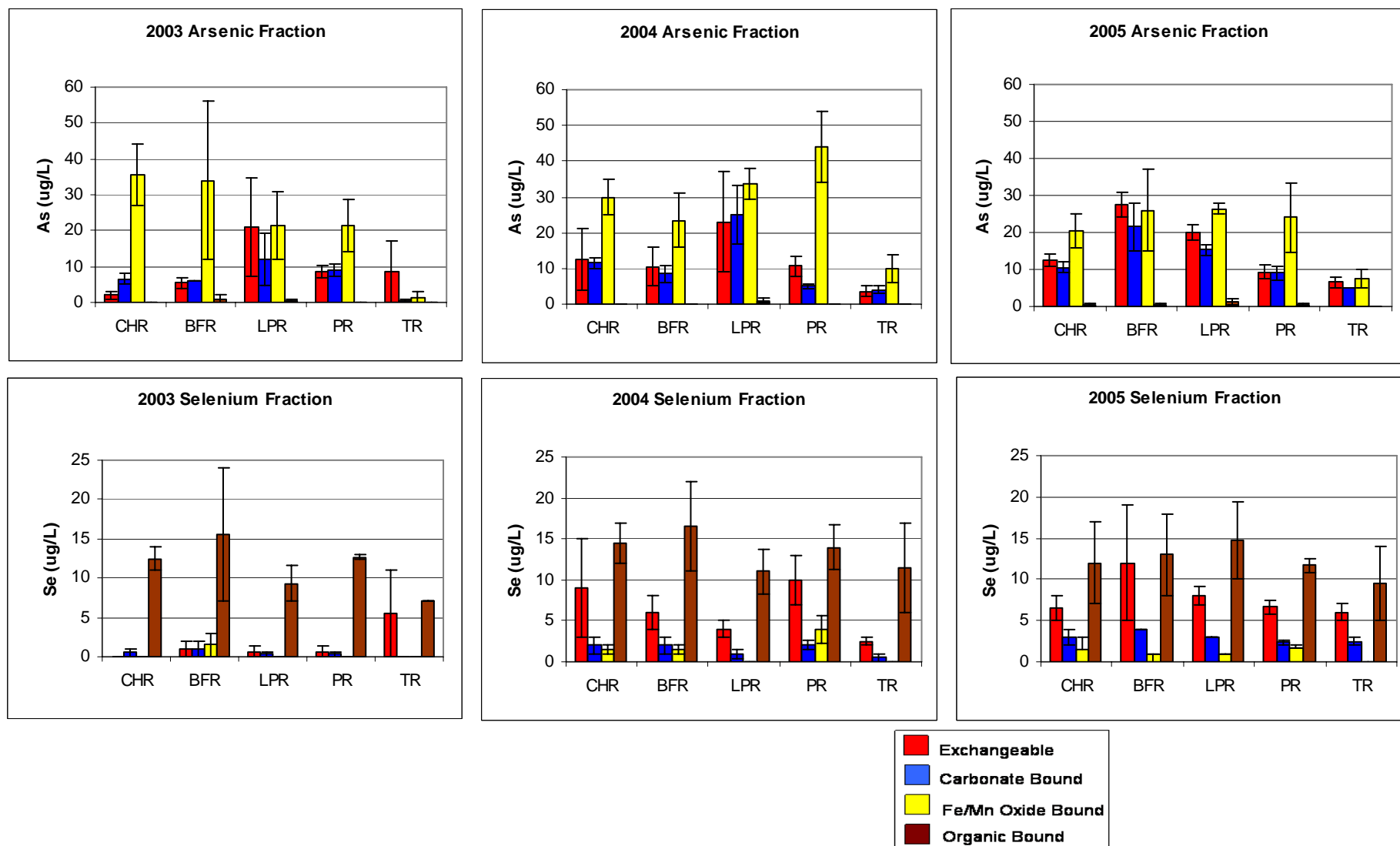
Figure 8. Average Arsenic and Selenium concentrations in Exchangeable, Carbonate bound, Iron/Manganese Oxide bound, and Organic bound fractions of CBNG discharge pond sediment.
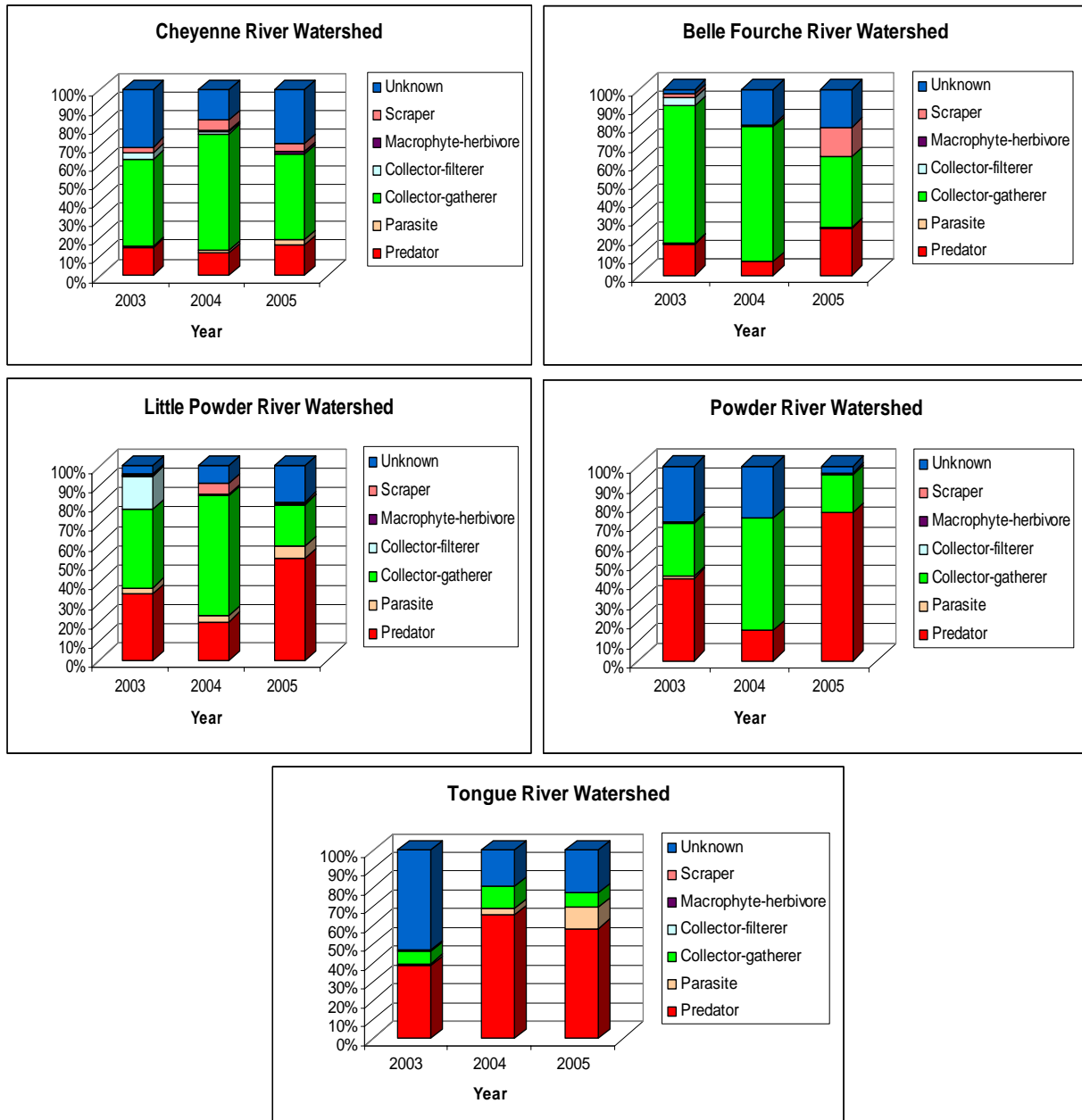
Figure 9. Aquatic macroinvertebrate community assemblages collected in CBNG discharge ponds in Cheyenne, Belle Fourche, Little Powder, Powder, and Tongue River watersheds from 2003, 2004, and 2005.

Table 1. Vegetation commonly encountered in and around CBNG discharge ponds in all watersheds.

Grasses	*Hordeum jubatum*
	Pascopyrum smithii
	Distichlis spicata
	Elytrigia intermedia
	Bromus japanicus
	Bromus tectorum
Grass-Like	*Juncus balticus*
	Scirpus meridimus
	Scipus americanus
	Carex parryana
Macrophytes	
	Polygonium amphibium
	Potomogeton pectanatus
Forbs	*Rupia maritima*
	Solanum rostratum
	Kochia scoparia
	Euphorbia humistata
	Astraglas bisulcatus
	Melilotus officinalis
	Cirsium arvense
	Cleome serrulata
	Grindelia squarrosa
	Xanthium strunarium